M.Sc. - (III - Sem)

Condensed Matter physics

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* PHYSICS *

UNIT - I

Unit cell:

It is simply like the cells and atoms which constitutes the bodies of living creatures and matter respectively.

Unit cell is the basic or smallest region (portion) of a crystal which when repeated by a number of times (or infinitely) in all directions builds the crystal lattice (crystal structure).

Unit cell always have minimum number of atoms or molecules for their formation. If not the cell or portion can not be considered as a unit cell.

Example:

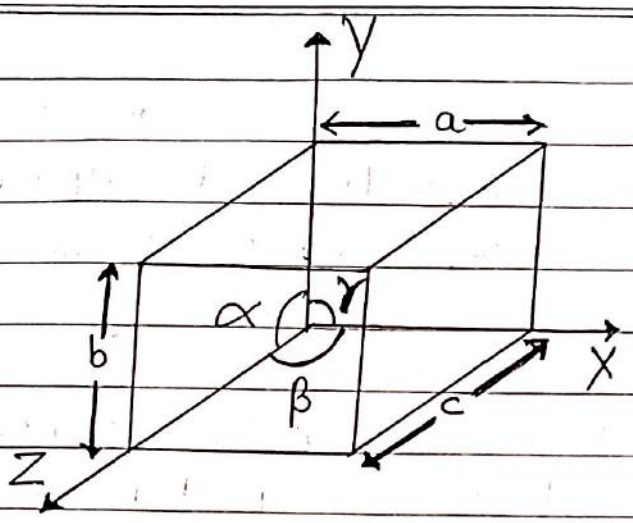
Considering a wall made of a number of bricks
→ Bricks may be considered as a unit cell.
→ Thus the wall so formed will be the crystal structure.

Crystal parameters:

There are following six parameters needed to describe a unit cell.

(i) The translation vectors (length of unit cell along the each crystallographic axes) $\vec{a}$, $\vec{b}$ & $\vec{c}$.

(ii) The angles b/w the crystallographic axes α, β and γ as shown in the figure on next page:

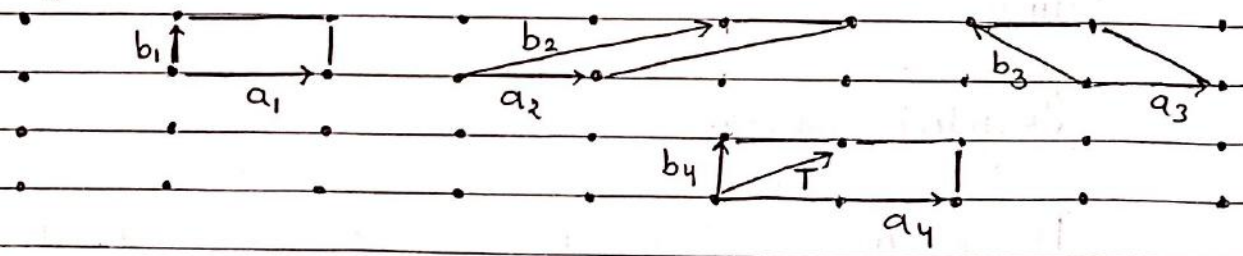


(iii) Crystallographic axis:

The lines (rays) OX, OY, OZ drawn mutually ⊥ to each other and parallel to the lines of any three faces (out of six) of the unit cell and do not lie in the same plane are called crystallographic axes.

→ Choice of a unit cell:

There may be a whole lot of arrangements in 3D crystal structure which are as shown below. ←



Now, there may arrise the following two type of cells (unit cells).

(i) Primitive unit cell:

A simple unit cell which has constituents of the

crystal present at the corners (lattice points) and have a minimum volume which can be shown to have a value,

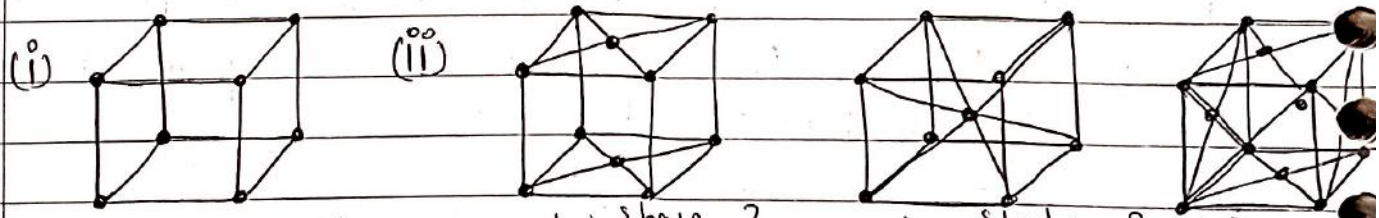
$$V_c = |\vec{a} \times \vec{b} \cdot \vec{c}|$$

Usually a primitive unit cell have only one lattice point (like scc) in it i.e one atom or molecule can be present at corners.

(ii) Non primitive unit cell:

A simple unit cell which has more than one lattice points (like fcc, bcc & hcp) per unit cell are called non primitive unit cell.

The can also be regarded or understood as "Centred unit cell".



Primitive unit cell.

Non-primitive unit cell

Examples:

Out of all the closed packed structures,

(i) Simple cubic cell - Primitive
(ii) face centred cell - Non primitive
(iii) base centred cell - Non primitive
(iv) body centred cell - Non primitive.

→ Now the answer to the question about the choice of unit cell is,

(i) In 3D the simplest "parallelopiped" formed by the primitive cell can be taken as the unit cell.

(ii) Acc. to the requirements we can also chose a non primitive cell.

For the vary (same) "purpose F.P Wigner and F. Seitz" provided a mechanism or method and the unit cell determined by this method is called "Wigner-Seitz unit cell"

For chosing a unit cell A/c to W-S process the following steps are used.

(i) First of all a refrence point is taken and then draw lines to connect this point to all nearby lattice points.

(ii) Draw new lines {If we have taken a plane} or planes {If we have taken a portion of space} bisecting each of the previous lines.

(iii) The smallest area (in plane lattice) or volume (in space lattice) enclosed by these lines gives the "W-S unit cell".

Examples:

If we follow the above mentioned procedure,

(a) The shape of a two dimensional "oblique lattice" is perfectly found to be "Hexagon"

(b) The shape of a 3D body centred cubic lattice is a "Trunkated (truncated) octahedron".

(c) The shape of a face centred cubic lattice is a "Rhombic dodecahedron".

Note:

An oblique lattice is a planer lattice which may be defined as "A lattice for which there is no restriction on the length of translation vectors $\vec{a}$ & $\vec{b}$ and the angle ϕ made between them for any arbitary a, b & ϕ".

✓ → Number of lattice points per unit cell:

The following relation is used to calculate the number of lattice point (if its density is known) in/of a unit cell.

$$a^3 = \frac{M n}{N \rho}$$

Where, M = Mass of n number of atoms
n = The number of atoms or lattice points
ρ = density of unit cell
N = Avagaddro's number
a^3 = Volume of the unit cell.
a = lattice constant.

The table on the next page (gradually) shows the same.

Symbol	Name	Additional points (Locations)	Total No. of lattice points
P	Primitive (scc)	—	1.
I	Body centred	Centre of the cell	2.
A	Base centred	centre of (1,0,0) face	2.
B		centre of (0,1,0) face	2.
C		centre of (0,0,1) face	2.
F	Face centred	centre of all faces {only one of each opposite pair}	4.
R	Rhombohedral	Diagonal of the cell Two points along the body	3.

Crystal structure : Various systems :

There are 32 classes of systems based on the geometrical considerations {i.e internal structure and symmetry}.

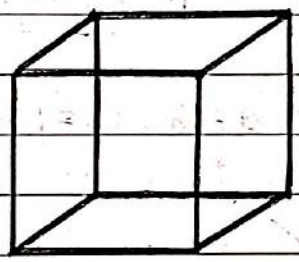
In general there are 7 groups of crystal systems which are also called "Basic systems" These are as follows,

1. Cubic (isometric)
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Trigonal (rhombohedral)
7. Hexagonal

These all systems can be differentiated on the basis of crystal parameters as shown in figure & table

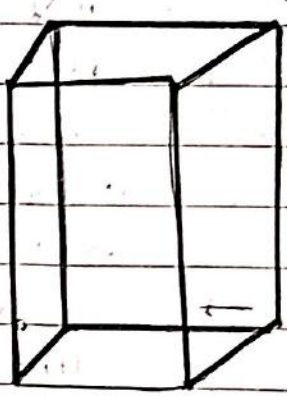
Serial Number	Crystal System	Axial length of unit cell	Interaxial angles	Examples.
1.	Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	Au, Cu, NaCl
2.	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	TiO_2, SnO_2, $NiSO_4$
3.	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	KNO_3, $BaSO_4$, $PbCl_2$
4.	Monoclinic	$a\neq b\neq c$	$\alpha=\beta=90^\circ\neq\gamma$	$CaSO_4 \cdot 2H_2O$, FeS
5.	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq90^\circ$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$
6.	Trigonal	$a=b=c$	$\alpha=\beta=\gamma\neq90^\circ$	As, Sb, Bi, Calcite
7.	Hexagonal	$a=b\neq c$	$\alpha=\beta=90^\circ$ & $\gamma=120^\circ$	SiO_2, Zn, Mg,

The corresponding geometrical structures are as given below.

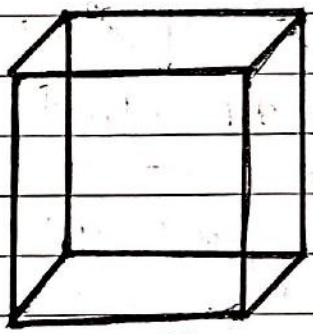


(i) Cubic crystal

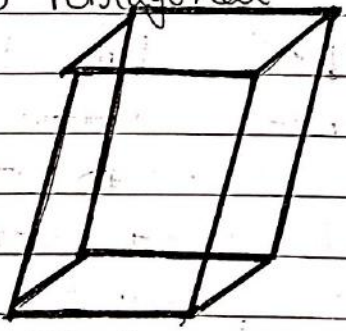
(ii) Tetragonal



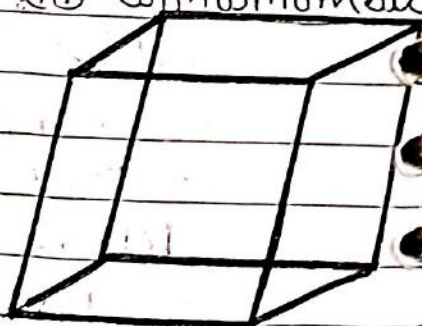
(iii) Orthorhombic



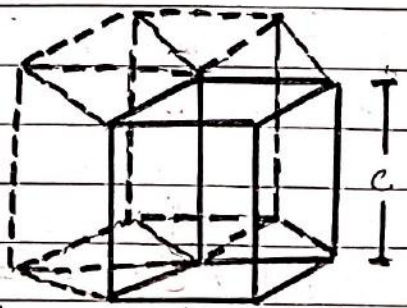
(iv) Monoclinic



(v) Triclinic



(vi) Trigonal

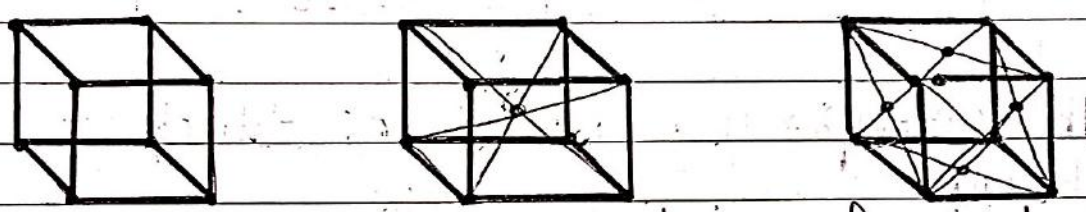


(vii) Hexagonal crystal.

Closed packed structures:- Bravais lattice

Bravais had pridicted or postulated that only 14 various arrangements of lattice are posible so that the lattide points can be arranged in space to have identical surroundings. These are refferred as "Bravais space lattice".

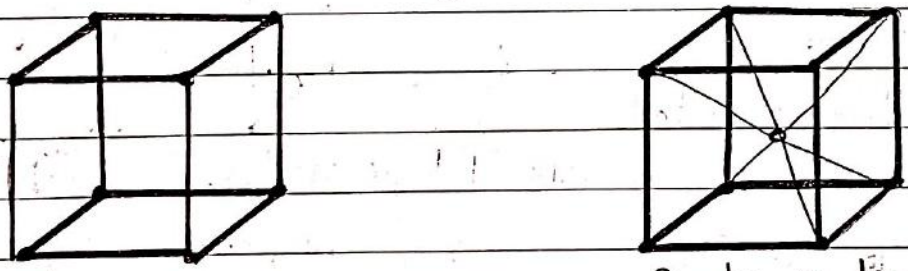
These are shown below =



(F.C.L)

Simple Body centred face centred

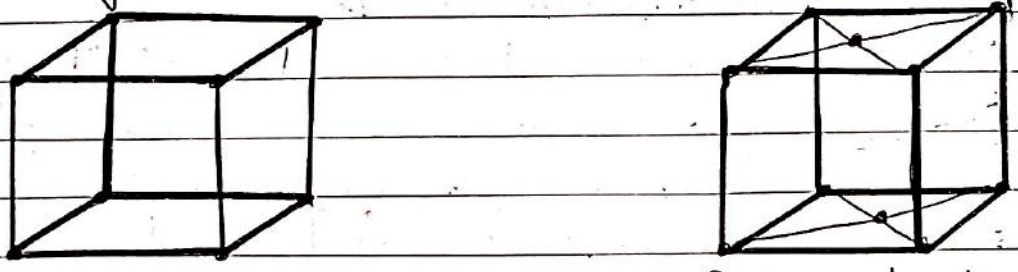
Simple cubic system $a=b=c$, $\alpha=\beta=\gamma=90°$



(B.C.L)

Simple Body centred

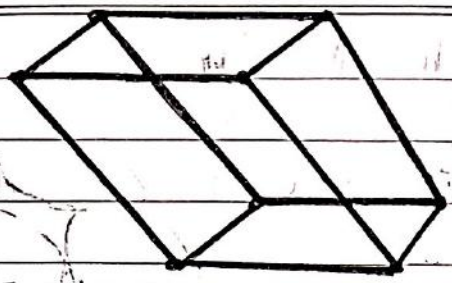
Tetragonal $a=b\neq c$, $\alpha=\beta=\gamma=90°$



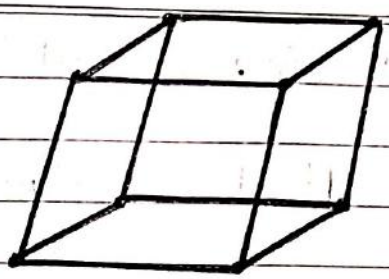
(B.L)

Simple Body centred

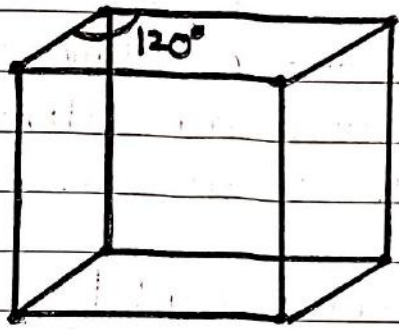
Monoclinic $a\neq b\neq c$, $\alpha=\beta=90\neq\gamma$



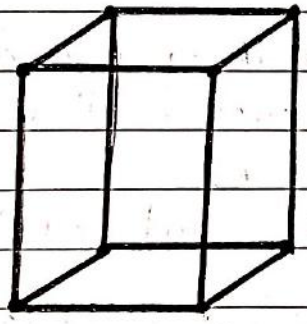
Triclinic $a \neq b \neq c$
$\alpha \neq \beta \neq \gamma$



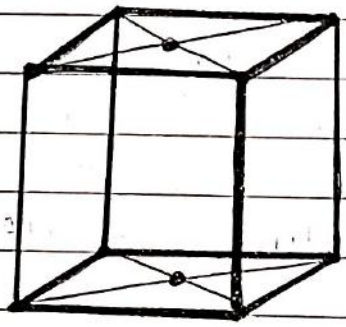
Trigonal $a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$



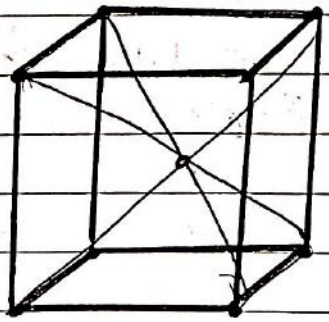
Hexagonal $a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$



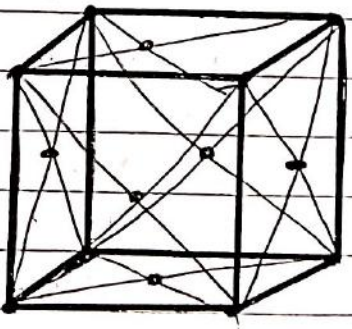
Simple



base centred



Body centred



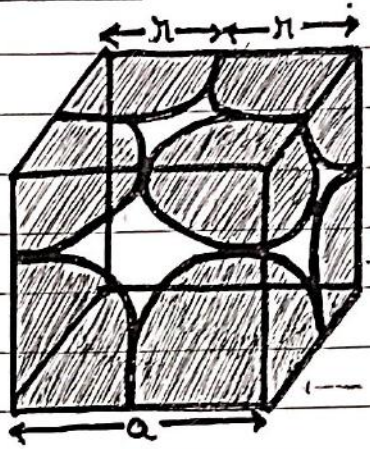
face centred

Orthorhombic $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

The close packed structures for metals (metallic crystal structure) are all crystalline and are divided as,

(1) Simple cubic (Scc) crystal structure :-

It has following specifications,



(i) One lattice point at each of the corners of the unit cell.

(ii) Coordination number (Number of surrounding neighbour atoms) is 6 in simple cubic cell.

i.e $\boxed{a = 2r}$

(iii) In simple cubic crystals the number of atoms i.e lattice pt. is $\frac{1}{8} \times 8 = 1$. (Where, a is called the lattice const.)

(iv) This type of structure is very open and loosely-packed i.e a lot of empty space is there.

(v) Volume of all the atoms in unit cell is,

$$\boxed{V = 1 \times \frac{4}{3}\pi r^3}$$

} 1 is multiplied to show the number of lattice points

(vi) Volume of unit cell (cube)

$$\boxed{V = a^3 = (2r)^3 = 8r^3}$$

(vii) Packing factor or density of packing is,

$$P.F = \frac{v}{V} = \frac{4/3\,\pi r^3}{8_2 r^3} = \frac{\pi}{6} = 0.52$$

or, $\boxed{P.F = 52\%}$

(viii) Only Polonium (Po) crystalizes in Sc structure

Note:

(i) Coordination number may be considered, directly proportional to the closely packed nature of structure.

(ii) Atomic packing factor may be defined as the ratio volume of atoms occupying the unit cell to the volume of unit self.

$$\boxed{P.F = \frac{v}{V}}$$

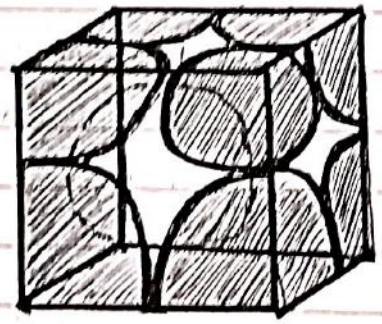
(2) Body centred cubic (bcc) structure:

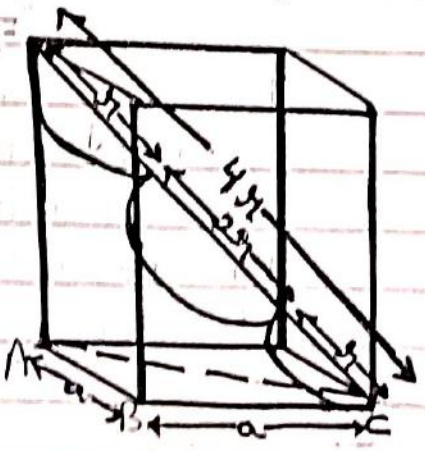
It has the following specifications.

(i) In bcc there are two lattice points per unit cell.

(a) 1. at the centre where all the diagonals meet.

(b) 1 is similar to scc due to the contribution of 8 corners





(ii) The coordination number is 8

(iii) Volume of all the atoms in bcc is,

$$\boxed{v = \frac{2 \times 4}{3} \pi r^3}$$

(iv) Volume of the bcc unit cell is given as,

$$\boxed{V = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}}$$

(v) Packing fraction or density of packing is

$$P.F = \frac{v}{V} = \frac{8/3\ \pi r^3}{64/3\sqrt{3}\ r^3} = \frac{\sqrt{3}}{8}\pi = 0.68$$

or, $\boxed{P.F = 68\ \%}$

(vi) Examples of bcc structure are crystalites of Fe, Cr, Mo, W and also alkali metals as K, Li, Na, Rb and Cs.

Note :

1. Calculation for lattice constant is as follows.

In $\triangle ABC$, $AC^2 = a^2 + a^2 = 2a^2$

In $\triangle CAF$, $CF^2 = (\sqrt{2}a)^2 + a^2 = 2a^2 + a^2 = 3a^2$

But, $CF^2 = (4r)^2 = 16r^2$

$\therefore 16r^2 = 3a^2$

$$\boxed{a = \frac{4r}{\sqrt{3}}}$$

2. In some cases the centre of the cube is occupied by one type of atoms and the corners are occupied by the others in a bcc structure This is called "Cesium chloride structure". It is discused later.

✓ → Closest packing :

X

The metals have identical atoms (Property of all elements as they are pure substances), hence there may be divisons on the basically layered structures

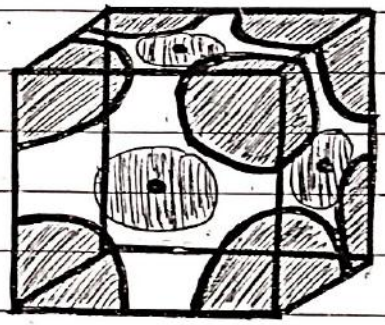
(i) Face centred cubic
(ii) Hexagonal close packing

Thus a closest packing may be defined as "A way or method of arranging equi-dimensional ojects in space such that the total available space is filled more efficiently (maximum)."

It can only be acheived (only when) by placing each available object in contact with the maximum number of like objects.

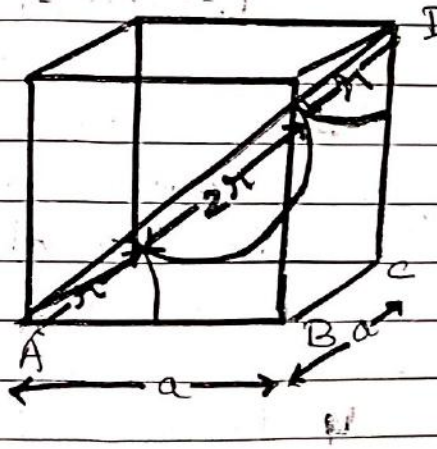
(3) Face centred cubic (fcc) structure :

It has following specifications,



(i) In fcc, the total number of lattice points (atoms) are 4.

(ii) The coordination number in fcc is 12



(iii) Volume of the atoms in the unit cell,

$$V = 4 \times 4/3 \pi r^3$$

(iv) Volume of the unit cell is,

$$V = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \frac{64r^3}{2\sqrt{2}}$$

(v) Packing fraction or density of packing is,

$$P.F = \frac{v}{V} = \frac{16/3 \pi r^3}{64/3\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

or, $\boxed{P.F = 74\%}$

(vi) Examples of fcc structure are crystalites of Cu, Ag, Au, Al, Ni, Pd and Pt.

Note :

1 The 4 lattice points in fcc are because,

(a) 3. because of the contribution of six faces as each face has a lattice point at its centre. i.e $6 \times \frac{1}{2} = 3$

(b) 1 because of contribution of 8 lattice points present at the corners (similar to sec).

2. Calculation of lattice constant is as follows,

In the figure, $(4r)^2 = a^2 + a^2$

$16r^2 = 2a^2$

$\boxed{a = 2\sqrt{2} r}$

3. In fcc atoms touch each other along the face diagonals.

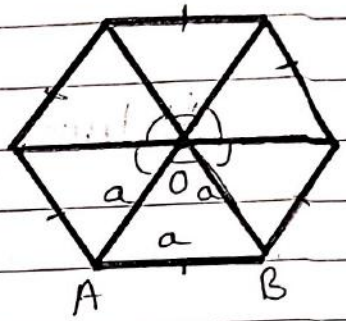
(4). Hexagonal close packed (hcp) structure. :

It has following specifications,

(i) Its coordination number is same as of fcc i.e 12

Reason :

It is because in hcp each lattice is surrounded by 6 others in its own layer and 3 lattice points are each connected to it from the layer ~~above~~ below or above it.



Top view of hcp structure.

(ii) The number of lattice points per unit cell i.e the number of atoms in the cell are 6.

Reason

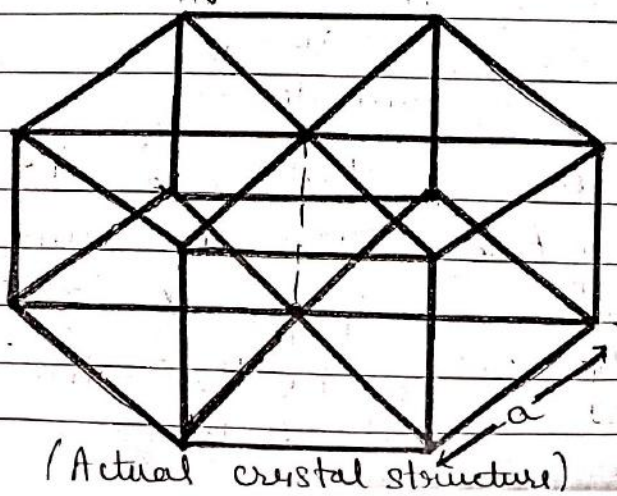
It is a combination of, $\boxed{\frac{3}{2} + \frac{3}{2} + 3 = 6}$

- Each layer has 7 atoms or lattice points
- Each corner atom is surrounded by 6 hexagon cells.
- The three of the atoms within the body are each shared by 2 surrounding cells.

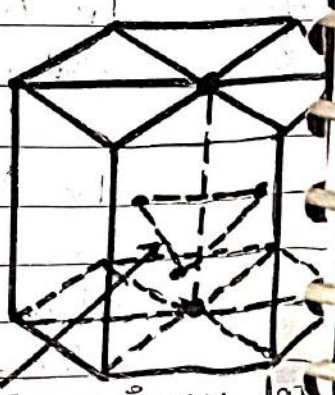
($\because \frac{3}{2}, \frac{3}{2}$ are the parts)

- The three atoms within the body of the cell are fully contributing to the cell.

The side view of hcp



(Actual crystal structure)



Three inner lattice points.

(iii) Volume of the atoms in the unit cell is

$$\boxed{V = 6 \times \frac{4}{3} \pi r^3}$$

(iv) Volume of the unit cell is,

$$V = \frac{3\sqrt{3}}{2} a^2 c \quad \{\text{Volume of hexagonal 3D structure}\}$$

Where $\boxed{c = \frac{2\sqrt{2}}{\sqrt{3}} a}$ & $\boxed{a = 2r}$

(v) Packing fraction or density of packing is

$$P.F = \frac{v}{V} = \frac{8\pi r^3}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

or, $\boxed{P.F = 74\%}$

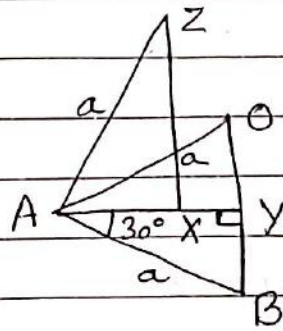
(vi) Examples of hcp structure are crystallite of Mg, Zn, Cd, Ti and Ni.

Note:

(i) Calculation for the ratio c/a is as follows

In ΔABY

$AY = \frac{\sqrt{3}}{2} a$ $\{\because \Delta ABY$ is equilateral$\}$



In ΔAXZ

$\boxed{XZ^2 + AX^2 = AZ^2}$ — (I)

also,

$\boxed{AX = \frac{2}{3} AY}$ $\{$Centroid of a Δ divides the median into 2:1$\}$

$$\therefore AX = \frac{2}{3} \times \frac{\sqrt{3}}{2} a = \frac{a}{\sqrt{3}}$$

Then, eqn (I) will become

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 \quad \{ c/2 \text{ is taken as whole } c \text{ is not in } \Delta \}$$

$$\Rightarrow c^2 = \frac{8}{3} a^2$$

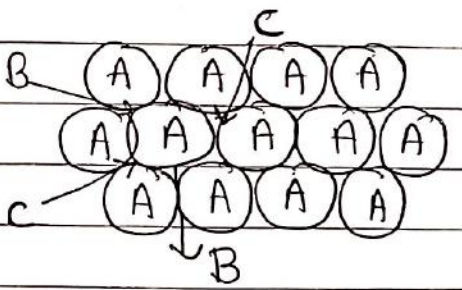
$$\Rightarrow \boxed{c = \frac{2\sqrt{2}}{\sqrt{3}} a}$$

(ii) The P.F of hcp and fcc are both 74% (maximum) and hence they are called "closest packing"

(iii) The hcp atoms do not touch each other along the face diagonals.

→ **Explanation of HCP & FCC Structures:**

Let us consider atoms to be solid spheres (hard) as shown alongside.



Then there may be two arrangements possible.

(i) HCP (hexagonal closed packing)
(ii) FCC (face centred cubic)

(B and C are Placed alternatively to each other)

In the layered structure, the bottom layer spheres are arranged by placing each sphere in contact with six others (say position A).

Such layer can be called "Basal plane" of hcp

or (1,1,1) plane of fcc structure.

Now, Second layer has an option of taking positions marked as B_s or C_s, say it occupies those marked as B_s.

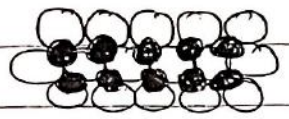
There is a question that "Where can the third layer be placed"? The answer to this is the explanation of hcp & fcc structure.

(a) **HCP structure.** When the third layer is placed at the position of A_s (i.e. of first layer) and fourth layer is placed at the position of B_s (i.e of second layer). This Gives a form ABABAB..... (or equivalently for C in place of B as ACACAC.....)

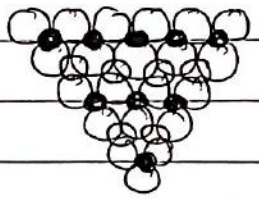
It has a hexagonal primitive cell in which "basis" contains 2 atoms, 1 at origin (0,0,0) and the other at $\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}\right)$.

(b) **FCC Structure.** When the third layer is placed at the vacant (only) spaces marked as C and fourth, fifth and sixth layers are again following the same pattern i.e ABC ABC ABC.....

In fcc, unlik hcp which has only one plane (i.e basal plane) there are four equivalent planes. The closed packed layers are the body diagonal planes of cube.



{ Representation of HCP cubic structure }



{ Representation of fcc cubic structure }

→ Some other structures :

1. Diamond cubic structures :

It has got the following specifications.

(i) The number of lattice points per unit cell are 8.

(ii) The volume of the atoms in the unit cell are,

$$\boxed{V = 8 \times \frac{4}{3}\pi r^3}$$

(iii) The volume of the unit cell is,

$$\boxed{V = a^3 = \left(\frac{8r}{\sqrt{3}}\right)^3 = \frac{512}{3\sqrt{3}} r^3}$$

(iv) The packing fraction or density of packing is

$$P.F = \frac{v}{V} = \frac{\frac{32}{3}\pi r^3}{\frac{512}{3\sqrt{3}} r^3} = \frac{\sqrt{3}\pi}{16} = 0.34$$

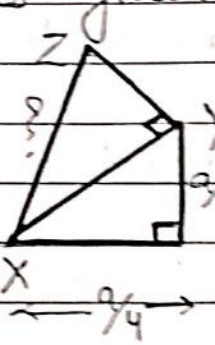
or $\boxed{P.F = 34\%}$

Thus, diamond structure has a lot of free space and is a loosely packed structure.

(v) Examples of diamond structure are crystalites of Si, Ge, gray Sn apart from diamond (an allotropic form of carbon) itself.

Note :

1. Calculation of lattice constant is given as,



In $\triangle XYZ$, $XY^2 = \frac{a^2}{4^2} + \frac{a^2}{4^2}$

$$= \frac{a^2}{8}$$

& $XZ^2 = \frac{a^2}{8} + \frac{a^2}{16}$

$$= \frac{3}{16} a^2$$

also, $XZ = a = 2r$

$\therefore$ $(2r)^2 = \frac{3}{16} a^2$

$$a^2 = \left(\frac{8}{\sqrt{3}} r\right)^2$$

or, $$\boxed{a = \frac{8r}{\sqrt{3}}}$$

2. For explanation of diamond structure, let us consider each atom to be at the centre of tetrahedron with its four nearest neighbours at the four corners of the tetrahedron.
It can be observed that if the central atom of the tetrahedron fcc sublattice the four corners are occupied by any other sublattice.
Further, as all atoms are equivalent therefore each of them can be treated as being the centre atom of the tetra-

→ **Zinc blende Structure :**

In this type of structure the atoms are not equivalent and are also different in size {Size of cation and anion is different} but the atoms still are able to constitutes a similar tetrahedron structure as in case of diamond.

It is basically resembling with 3-5 semiconducting crystals such as InSb, GaAs, GaP.

In Zinc blende structure,

(i) Zn atoms are placed on one fcc lattice
(ii) S atoms are placed on the other fcc lattice
(iii) Structure resembles with that of fcc and diamond.

→ **Sodium chloride structure (rock-salt structure) :**

Sodium chloride is basically an ionic compound, Thus in NaCl crystal there is a electrostatic force involved between Na^+ and Cl^- ions. Also arrangement of Na^+ & Cl^- ions cause repulsion between outermost shells of these ions {both have electrons and hence will repel each other}.
Because of this attraction and repulsion (one followed after the other) an equilibrium is achieved which provides stability to this structure

In this structure, each ion is surrounded by six nearest neighbours of the opposite kind. Thus its coordination number is six.

Examples of NaCl structure are crystallites of KCl, KBr, MgO, AgBr, other alkali halides etc

→ In NaCl structure,

(i) Na^+ and Cl^- ions are seperated by ½ (half) of body diagonal of the unit cell.
(ii) It resembles with the fcc.
(iii) The position of Na^+ and Cl^- ions in NaCl is,

Na^+ : $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$

Cl^- : 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$

These are planer notation discused earlier.

→ Cesium chloride structure :

It is different from that of NaCl structure as,

(i) It has a coordination number 8.
(ii) In cesium chloride one type of ions are situated at the body diagonal (bcc structure)
(iii) It resembles with simple cubic structure in terms of its symmetry.

In cesium chloride structure,

(i) The positions of Cs^{2+} and Cl^- ions are as follows.

Cs^{2+} : 000

Cl^- : $\frac{1}{2}\frac{1}{2}\frac{1}{2}$